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# Silylation of carbon surfaces through the electrochemical reduction of 2,2'-bipy-R<sub>3</sub>SiCl adducts

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## Abstract

Electrochemical reduction of complexes of monochlorosilanes with redox-active ligands such as 2,2'-bipy occurs in one-electron fashion at moderately negative potentials,  $E \cong -1$  V vs SCE (in CH<sub>3</sub>CN/0.1 M Bu<sub>4</sub>NBF<sub>4</sub>), leading to silyl radicals. These radicals, trapped with  $\alpha$ -phenyl-N-*t*-butyl-nitrone and characterized as spin-adducts by ESR spectroscopy, add to carbon interfaces (glassy carbon, graphite) providing an efficient method of covalent Si-C silylation of such surfaces. Silylated interfaces were studied by voltammetry, EIS, SEM, EDS, and FTIR spectroscopy.

## Keywords

Carbon silylation, silyl radicals, redox active ligands, bipyridine

## 1. Introduction

Silylation of solid materials is intensively sought for, in line with constantly growing technological demand [1]. Since such silylation usually needs an active hydrogen on the surface (in -OH, -NH and -SH groups), carbonaceous substrates and different forms of carbon (GC, graphite, HOPG, CNT) are least prone to surface silylation among such materials [2]. While carbon derivatization of oxide-free silicon surfaces is well developed [3], covalent Si-C silicon-to-carbon grafting (contrary to Si-O-C silylation e.g. of graphite-oxide [4] or of hydroxylated

MWCNT [5]) is quasi unknown. However, keeping in mind omnipresence of  $C_{sp^2}$  unsaturated inclusions practically in any carbon materials (making possible the very C-C radical grafting, see [6] and later works [7]), their radical silylation must well be possible. In fact, photochemical radical bisilylation of fullerenes was reported at the end of 90's [8] (for photochemical silylation of SWCN using  $(MeO)_3SiH$  and  $Ph_6Si_2$ , see [9]). We have recently proposed an efficient method of covalent grafting of silatranes to carbon interfaces [10] using Si-centered radicals issued from transition metal-catalyzed one-electron reduction of Si-Cl bond in chlorosilanes. Here we report a new, simple and general method of cathodic silylation of carbons based on one-electron reduction of *in situ* formed complexes of chlorosilanes with 2,2'-bipyridine (bipy). This procedure opens the way to various hydrolysis-stable silylated carbon materials for many areas of modern technology and research.

## 2. Experimental

A PAR-2273 potentiostat was used for voltammetry and large-scale silylation. The potentials are referred to SCE and corrected using  $E^0(Fc^+/Fc)$  system. A 2 mm GC disk sealed in a Pyrex tube with TorrSeal epoxy resin (Varian) was used as a working electrode. Silylation of larger electrodes (1-2  $cm^2$ ) was carried out in a 25 mL two-compartment cell separated with a sintered glass diaphragm and fitted with a 2.5×75 mm GC rod anode.

DMF or acetonitrile (Aldrich) containing 0.1 M of supporting electrolyte were used as working solutions. Analytical grade DMF (Aldrich) was passed through a column with activated (in vacuum overnight, 150 °C) neutral  $Al_2O_3$ ;  $CH_3CN$  was distilled from  $CaH_2$ . Liquid chlorosilanes (ABCR) were kept over Mg turnings and distilled prior to the electrolyses. 2,2'-Bipyridine (Aldrich) was additionally sublimed before using. The supporting electrolytes,  $Bu_4NPF_6$  or  $Bu_4NBF_4$  (Aldrich), were activated in vacuum at 80°C for 10 hours and kept over  $P_2O_5$ . All experiments were carried out under Ar atmosphere.

For EDS and SEM analyses, Jeol JSM 6301F and Jeol JSM 6400 (Oxford Link INCA) spectrometers have been used. EPR spectra were recorded using an X-band Bruker EMX (9.46 GHz, modulation frequency 100 kHz) spectrometer.

### 3. Results and discussion

Stable neutral complexes of 2,2'-bipyridine with iodo- and bromotriphenylsilanes were first reported by Corey and West [11]. Later, Kummer and colleagues prepared similar complexes with polychloro silanes, disilanes and disiloxanes [12-14]; however, as was pointed out already in first works [11], such adducts could not be formed with monochloro silanes. In contrast to this statement, the electrochemical response of 2,2'-bipyridine in the presence of polyhalo (for  $\text{SiI}_4$ , see [15]) and monochlorosilanes  $\text{R}_3\text{SiCl}$  [16] is quite similar. When a monochlorosilane is added to the solution of bipy (own reversible one-electron reduction at -2.1 V vs. SCE), a new redox system appears at up to 1 V less cathodic potentials (for  $\text{Et}_3\text{SiCl}$ ,  $E_p = -1.17$  V) as shown in Figure 1. For monochlorosilanes, this new system is assigned to  $(\text{bipy}\cdot\text{R}_3\text{SiCl})/(\text{bipy}\cdot\text{R}_3\text{SiCl})^\bullet$  couple. Similar anion radical complexes of 2,2'-bipy with poly- and monohalogermanes were recently reported [17].

The reduction peak current  $i_p$  is linear with  $\nu^{1/2}$  and corresponds to the transfer of one electron as shown by comparison with  $i_p(\text{Fc})$  and with  $it^{1/2}$  from one-step chronocoulometry. Even at moderately fast scan rates ( $\nu > 1\text{-}2$  V/s) the peak of reoxidation of the anion-radical complex  $(\text{bipy}\cdot\text{R}_3\text{SiCl})^\bullet$  can be observed practically for all chlorosilanes considered ( $\text{R} = \text{Ph}$ , vinyl, Me, Et, Pr) attesting reversible ET followed by a fast chemical reaction (scheme 1). Although not stable enough to be isolated in solid state, the anion-radical complexes of monochlorosilanes are formed in solution under the electrochemical conditions, favored by ET (from  $E_{\text{bipy}}^0 - E_{\text{bipy}\cdot\text{Me}_3\text{SiCl}}^0$ , the formation constant was roughly estimated as  $K < 8 \times 10^{10}$ ). Primary anion radicals  $(\text{bipy}\cdot\text{R}_3\text{SiCl})^\bullet$  could be directly detected by ESR spectroscopy while

secondary silyl radicals  $R_3Si^\bullet$  issued from their decay were trapped with  $\alpha$ -phenyl-N-*t*-butyl-nitrone (PBN) in the form of persistent spin adducts (Figure 2).

Consecutive scans between -0.5 and -1.2 V (scan rate  $\nu = 50 \text{ mV s}^{-1}$ ) cause remarkable electrode passivation, - the reduction peak of  $bipy \cdot R_3SiCl$  rapidly diminishes until its total disappearance (Figure 3). This process reflects rapid coverage of the electrode surface with  $R_3Si$  groups, covalently grafted via radical addition of  $R_3Si^\bullet$  radicals to reactive double bonds of  $C_{sp2}$  inclusions in GC. Thus prepared surfaces are chemically (in air or in contact with  $CH_3CN$ , THF,  $CH_2Cl_2$  and acetone) and mechanically (ultrasonic bath, ~3 min) stable. SEM of the silylated interfaces shows huge modification of the morphology of initially flat GC surfaces (Figure 4). Energy dispersion spectroscopy attests the presence of silicon in the grafted layer (Figure 5) and reflectance FTIR spectra show characteristic vibrations of alkyl groups at the surfaces silylated with  $PhMe_2Si$  and  $Et_3Si$ . Silylation remarkably increases the charge transfer resistance through the GC interface as was shown by electrochemical impedance spectroscopy (Figure 5). Interestingly, Nyquist plot for the oxidation of ferrocene at a  $PhMe_2Si$ -GC interface has complex shape corresponding to a nearly blocking electrode with relatively small bulk resistance and three different time constants ( $R_{CT} = 2.4, 11.6$  and  $24 \text{ k}\Omega$ , Figure 5).

The  $i_p m^{1/2} - m$  ( $m$  = number of scans) plot reveals at least three zones, corresponding to different grafting regimes (Figure 3): (a) linear with time increase of available electrode area probably owing to edge-addition of  $R_3Si^\bullet$  radicals partially splitting graphitic layers, (b) linear decrease of available surface resulting from the grafting to the formed  $R_3Si$ -framed flat areas followed by (c) clogging the holes in the formed  $R_3Si$  layer and its compacting to form a completed monolayer which ends the silylation. After this, the surface is totally blocked ( $i = 0$ ) and further grafting is no more possible.

Taking the radius of  $Et_3Si$  footprint on an ideally flat surface as  $3.8 \text{ \AA}$ , the monolayer coverage is expected to be at  $\Gamma_{max} = 4.87 \times 10^{-10} \text{ mol cm}^{-2}$  corresponding, in terms of one-electron character of grafting, to  $4.7 \times 10^{-5} \text{ C cm}^{-2}$ . Quite reproducible coulometry of grafting to GC at

different scan rates,  $Q_{\max} = (6.9 \pm 0.4) \times 10^{-4} \text{ C cm}^{-2}$ , suggests that the ratio of experimental-to-theoretical values of ca. 15 is not so much related to the current efficiency of generation of radicals as to roughness of the obtained surface (see Figure 4). Natural graphite can as well be silylated in this process; however roughness of the surface, depending on sample preparation, and degree of exfoliation accompanying the grafting, which varies with the scan rate, are more difficult to quantify. The interfaces silylated this way have no Si-O bonds and therefore do not "leak" like alkoxysilylated interfaces.

#### 4. Conclusion

One-electron cleavage of Si-Cl bond in complexes of 2,2'-bipy with monochlorosilanes provides a convenient way for generating silyl radicals in the immediate vicinity of the electrode which favors their efficient addition to the unsaturated zones in glassy carbon. Considering the electrode as electron-donor and nucleophile, the situation resembles to the facilitation of nucleophilic reactions of halosilanes by silicophilic co-reagents inducing pentacoordination of silicon and rendering it more reactive [18]. Thus, bipy-assisted silylation of carbon interfaces, free of inconvenience of pre-deposition of subnanolayers of transition metals, can be applied to a many commercially available mono- and poly-halo (Hal = Cl, Br, I) silanes. Similar anion radical complexes with 2,2'-bipy were recently reported for halogermanes [17]. Electrode passivation during their reduction, caused by the same phenomenon, means that germanium-to-carbon covalent grafting (via Ge-C bonds) can also be effected in the similar way. Further works in this field are underway.

#### Acknowledgement

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## Figure captions

Figure 1.

(a) Voltammetry of 2,2'-bipyridine ( $3 \text{ mmol L}^{-1}$ ) alone (1) and in the presence of  $\text{Me}_3\text{SiCl}$  (2 and 3:  $1$  and  $2 \text{ mmol L}^{-1}$ ). Anodic signals of equal intensity (curves 2, 3) correspond to the oxidation of  $\text{Cl}^-$  eliminated in the cathodic step. (b)  $\text{Bu}_4\text{NCl}$  ( $1.5 \text{ mmol L}^{-1}$ ). AN/ $0.1 \text{ M Bu}_4\text{NPF}_6$ ;  $\nu = 500 \text{ mV s}^{-1}$ .

Figure 2.

(A) Real-time ESR of  $(\text{bipy} \cdot \text{Et}_3\text{SiCl})^\bullet$  electrogenerated at  $E = -0.85 \text{ V}$  in AN/ $0.1 \text{ M Bu}_4\text{NPF}_6$  ( $g = 2.0037$ ,  $a_N = 2.448 \text{ G}$ ,  $a_H = 4.888, 1.678, 0.671, 0.655 \text{ G}$ ). (B) Ex-cell ESR spectra of the spin adduct of  $\text{Et}_3\text{SiCl}$  with PBN formed in the electrolysis of  $\text{bipy}/\text{Et}_3\text{SiCl}$  ( $1:1 \text{ eq}$ ) in the presence of PBN at  $-0.8 \text{ V}$  in AN/ $0.1 \text{ M Bu}_4\text{NBF}_4$  ( $g = 2.0047$ ,  $a_N = 14.749 \text{ G}$ ,  $a_H = 3.263 \text{ G}$ ).  $T = 21^\circ\text{C}$ . (a) experimental, (b) simulated spectra.

Figure 3.

(A) Recurrent scans of the reduction of  $\text{bipy} \cdot \text{Et}_3\text{SiCl}$  and (B) the coulometry of grafting. AN/ $0.1 \text{ M Bu}_4\text{NBF}_4$ .  $\nu = 100 \text{ mV s}^{-1}$ . (C) Evolution of Cottrell term of  $i_p$  with number of scans.

Figure 4.

SEM of bare (upper) and triorganosilyl-grafted (lower) zones of GC plates at similar magnifications.  $\text{PhMe}_2\text{Si-GC}$ ,  $\times 2 \times 10^4$  (A) and  $\times 5 \times 10^4$  (B).  $\text{Et}_3\text{Si-GC}$ ,  $\times 5 \times 10^4$  (C).

Figure 5.

(A) EDS analysis of  $\text{Et}_3\text{Si-GC}$  interface. (B) Nyquist plot for oxidation of  $\text{Fc}$  ( $3.5 \text{ mmol L}^{-1}$ ) in AN/ $0.1 \text{ M Bu}_4\text{NBF}_4$ . Frequency from  $0.76 \text{ MHz}$  to  $575 \text{ } \mu\text{Hz}$ ,  $E_{\text{app}} = 0.3 \text{ V}$ ,  $\Delta E = 10 \text{ mV}$ . Inset: oxidation of  $\text{Fc}$  at bare (1) and at  $\text{PhMe}_2\text{Si}$ -modified (2) electrode. (C) FTIR spectra of  $\text{Et}_3\text{Si}$ - and  $\text{PhMe}_2\text{Si}$ -modified electrodes. A:  $2960\text{-}2850 \text{ cm}^{-1}$   $\nu(\text{CH}_3)$ , B:  $1430\text{-}1370 \text{ cm}^{-1}$   $\delta(\text{C-H})$ , C:  $1260, 1110 \text{ cm}^{-1}$   $\nu(\text{Si-C})$ , D:  $730 \text{ cm}^{-1}$   $\delta(\text{C-H}) \text{ Ph}$ .



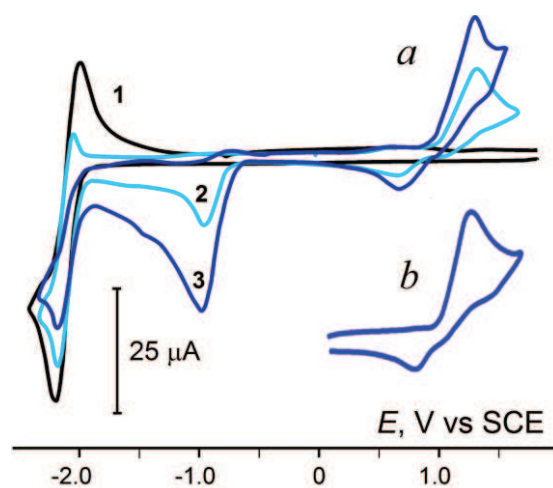


Figure 1.

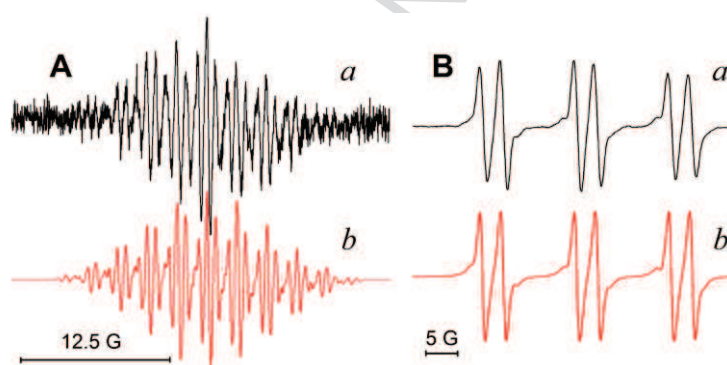


Figure 2.

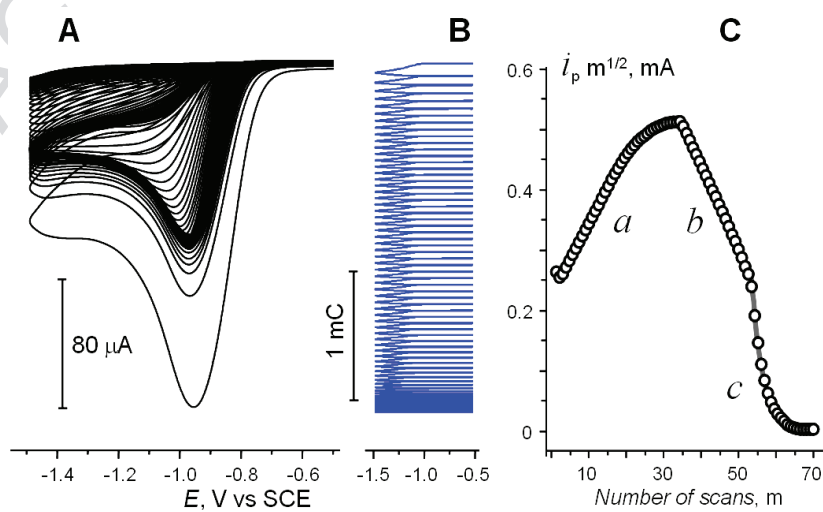


Figure 3.

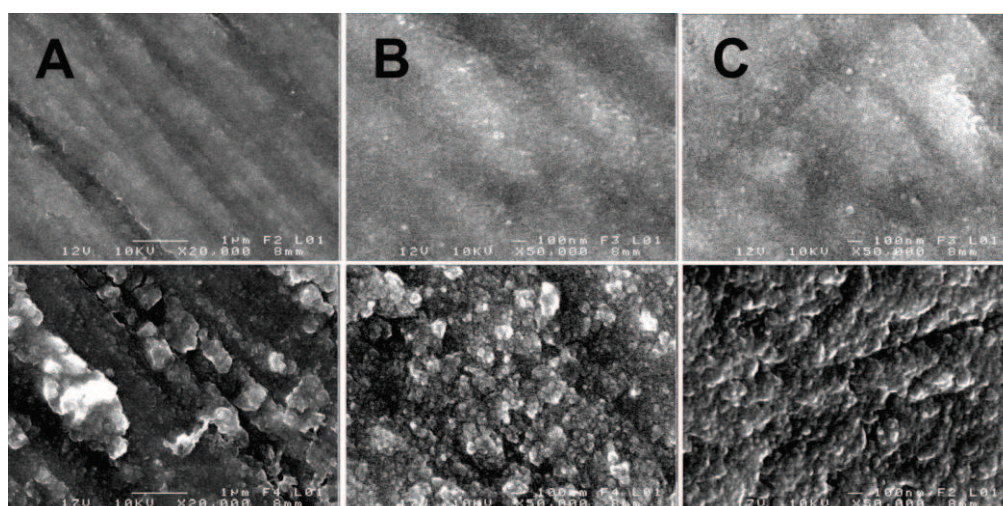


Figure 4.

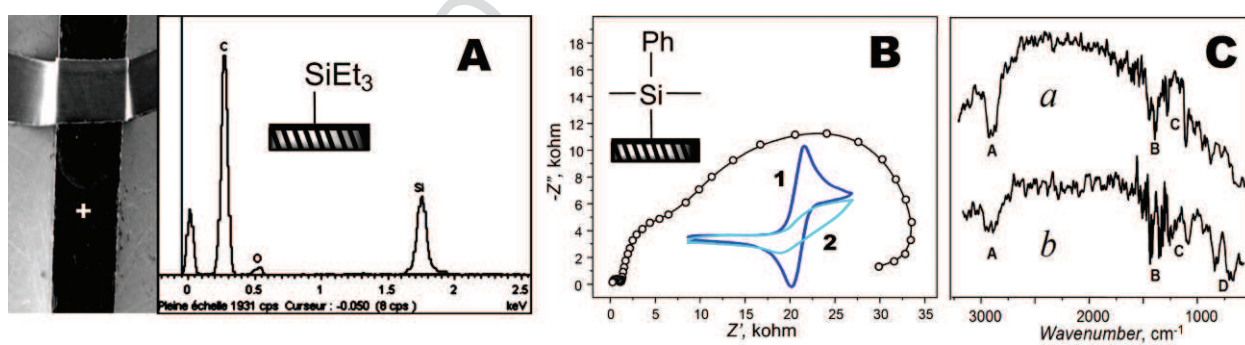
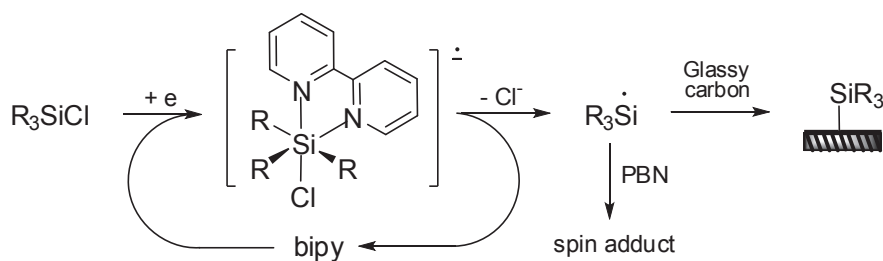


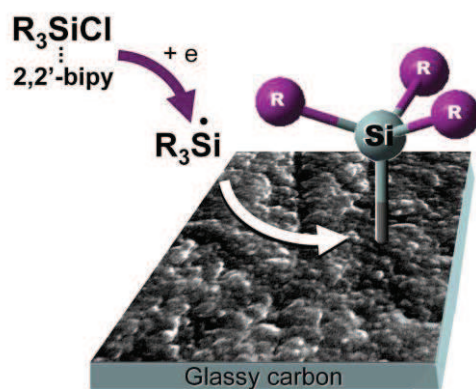
Figure 5.



Scheme 1

**Graphical abstract**

For "Silylation of carbon surfaces through the electrochemical reduction of 2,2'-bipy·R<sub>3</sub>SiCl adducts" by M. Dieng, J. Simonet, V. Jouikov



"Silylation of carbon surfaces through the electrochemical reduction of 2,2'-bipy-R<sub>3</sub>SiCl adducts"

By M. Dieng, J. Simonet, V. Jouikov

## Highlights

- 2,2'-Bipyridine forms adducts with monochlorosilanes in solution
- Anion radicals of bipy-mono-chlorosilane adducts are formed via one-electron reduction
- Cleavage of anion radicals of bipy-mono-chlorosilane results in silyl radicals
- Efficient addition of triorganosilyl radicals to carbon surface